



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
PREVENTION, PESTICIDES
AND TOXIC SUBSTANCES

Note to Reader

Background: As part of its effort to involve the public in the implementation of the Food Quality Protection Act of 1996 (FQPA), which is designed to ensure that the United States continues to have the safest and most abundant food supply.

EPA is undertaking an effort to open public dockets on the organophosphate pesticides. These dockets will make available to all interested parties documents that were developed as part of the U.S. Environmental Protection Agency's process for making reregistration eligibility decisions and tolerance reassessments consistent with FQPA. The dockets include preliminary health assessments and, where available, ecological risk assessments conducted by EPA, rebuttals or corrections to the risk assessments submitted by chemical registrants, and the Agency's response to the registrants' submissions.

The analyses contained in this docket are preliminary in nature and represent the information available to EPA at the time they were prepared. Additional information may have been submitted to EPA which has not yet been incorporated into these analyses, and registrants or others may be developing relevant information. It's common and appropriate that new information and analyses will be used to revise and refine the evaluations contained in these dockets to make them more comprehensive and realistic. The Agency cautions against premature conclusions based on these preliminary assessments and against any use of information contained in these documents out of their full context. Throughout this process, If unacceptable risks are identified, EPA will act to reduce or eliminate the risks.

There is a 60 day comment period in which the public and all interested parties are invited to submit comments on the information in this docket. Comments should directly relate to this organophosphate and to the information and issues available in the information docket. Once the comment period closes, EPA will review all comments and revise the risk assessments, as necessary.

These preliminary risk assessments represent an early stage in the process by which EPA is evaluating the regulatory requirements applicable to existing pesticides. Through this opportunity for notice and comment, the Agency hopes to advance the openness and scientific soundness underpinning its decisions. This process is designed to assure that America continues to enjoy the safest and most abundant food supply. Through implementation of EPA's tolerance reassessment program under the Food Quality Protection Act, the food supply will become even safer. Leading health experts recommend that all people eat a wide variety of foods, including at least five servings of fruits and vegetables a day.

Note: This sheet is provided to help the reader understand how refined and developed the pesticide file is as of the date prepared, what if any changes have occurred recently, and what new information, if any, is expected to be included in the analysis before decisions are made. **It is not meant to be a summary of all current information regarding the chemical.** Rather, the sheet provides some context to better understand the substantive material in the docket (RED chapters, registrant rebuttals, Agency responses to rebuttals, etc.) for this pesticide.

Further, in some cases, differences may be noted between the RED chapters and the Agency's comprehensive reports on the hazard identification information and safety factors for all organophosphates. In these cases, information in the comprehensive reports is the most current and will, barring the submission of more data that the Agency finds useful, be used in the risk assessments.

A handwritten signature in black ink, appearing to read 'J. Housenger', is written over the typed name and title.

Jack E. Housenger, Acting Director
Special Review and Reregistration Division

PC Code 121301

DRINKING WATER ASSESSMENT

SUBJECT: Drinking Water Assessment of Chlorpyrifos
PC Code:

TO: Steve Knizner
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THRU: Daniel Rieder
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DATE: November 13, 1998

The Environmental Fate and Effects Division has been requested to generate a Drinking Water Assessment for chlorpyrifos. This memorandum provides our best scientific judgement on the distribution of chlorpyrifos residues in water that may be used for drinking water based on Tier 1 and Tier 2 modeling (using GENEEC 1.2, PRZM 2.3-EXAMS, and SCI-GROW 1.0) and an assessment of existing ground- and surface-water monitoring data for chlorpyrifos. Limitations and assumptions for the models used have been presented in the chlorpyrifos Reregistration Eligibility Document and will not be repeated here.

Exposure Level Summary:

EFED has developed the best possible estimates given the available data, but without substantial additional research there will remain significant uncertainties in these assessments. The following caveats apply to these estimates:

- (1.) The estimates are intended to be as realistic as possible but apply only to the most vulnerable populations, existing monitoring data implies that the majority of the U.S. population will not be exposed at these levels.
- (2.) All of the estimates below are for unfinished water, some treatments could reduce the level of chlorpyrifos in finished drinking water (activated charcoal, for example, would be likely to remove some chlorpyrifos because it is easily adsorbed).
- (3.) Based on the existing monitoring database which covers a large part of the U.S., we believe the exposure estimates below are moderately conservative (i.e., exceed actual exposure by a several-fold factor) for a majority of the U.S. population. However, it must be emphasized that estimated exposure levels from these datasets incorporate data from some areas where chlorpyrifos usage is probably very low; residues in surface waters could be much higher in some areas if chlorpyrifos usage is more pervasive in the watershed.

The exposure estimates below are in four categories: flowing surface waters, lakes and reservoirs, ground water from non-termiticidal uses, and ground water from termiticidal uses. Summary numbers are:

Drinking Water Source	Exposure Duration	Chlorpyrifos	TCP
Ground water, except where termiticidal applications occur.	acute or chronic	0.1	86
Ground water, termiticide use areas.	acute or chronic	2000	>2000 ¹

Surface water, stream and rivers	chronic	0.4	4.6 to 304.3 ²
Surface water, reservoirs and lakes	chronic	0.4 to 6.7	4.6 to 304.3 ²
Surface water, stream and rivers	acute	0.4	4.6 to 404.2 ²
Surface water, reservoirs and lakes	acute	0.4 to 31.0	4.6 to 404.2 ²

¹ This estimate for TCP in ground water because of the termiticide use is highly uncertain because there are no monitoring data and the screening models cannot be appropriately applied to predict impacts from this type of use.

² All surface water estimates for TCP are highly uncertain because of the lack of any monitoring data. Actual concentrations are probably considerably lower than modeled values (the upper value for each estimate) primarily because the percent acres treated with chlorpyrifos in any watershed is expected to be much lower than 100% assumed in the modeling {i.e., probably in the vast majority of cases, the % of a watershed's land area treated is likely to be less than 5 or 10% because (1) chlorpyrifos is typically applied to less than 10% of the acreage for the two major crops, alfalfa and corn; (2) while chlorpyrifos is used more frequently on other crops, these crops have very small acreages nationally; and (3) the major non-agriculture use, for termite control, is typically injected in soil and runoff from this use is expected to be small. Refer to the use characterization section for details.}

Part 1: Ground Water Exposure Levels (Except Termiticidal Uses).

Chlorpyrifos exposure from agricultural uses is not expected to exceed $0.1 \mu\text{g L}^{-1}$ (upper-bound, 99+ percentile exposure level based on SCI-GROW modeling compared to United States survey data), with most monitoring results show only occasional contamination of ground water at a level of $0.04 \mu\text{g L}^{-1}$ or less (Table 7; refer to the section entitled "Conclusions on Likely Drinking Water Exposure Levels" for further details). An exception to this conclusion is the termiticidal uses, discussed below.

No ground-water monitoring data are available for the major chlorpyrifos degradate 3,5,6-trichloro-2-pyridinol (TCP), but modeling based upon existing monitoring data for other pesticides in vulnerable ground water indicates that TCP residues may range up to $86 \mu\text{g L}^{-1}$ in shallow ground water used for drinking water. Residues would of course, likely be much lower in less vulnerable ground water.

Part 2: Ground Water Exposure Levels - Termiticide Uses.

Chlorpyrifos exposure from termiticidal use is highly localized and usually only in wells located within 100 feet of the treatment area. Measured chlorpyrifos residues have ranged up to $2000 \mu\text{g L}^{-1}$, with chronic exposure levels unknown, but presumably significantly lower. Residues of TCP are likely to be higher and more persistent in ground water from termiticidal applications, however, no monitoring data and no modeling procedures are available for this type of use pattern. (Note: No separate exposure numbers have been calculated for this use for surface water since this is a highly localized and deeply incorporated use not as subject to surface runoff. This is, however, quantitatively a very significant use, with a recent estimate of seven million pounds constituting about 30% of the total annual use, c.f. Table 4).

Part 3: Surface Water Exposure Levels - Rivers and Streams.

Overall, the available monitoring data are quite extensive in terms of volume of samples collected and geographic extent of coverage. However, these data are not targeted specifically to chlorpyrifos use areas and information on chlorpyrifos usage in the watersheds sampled from is not readily available. A further limitation is that these monitoring data do not focus on the types of water bodies where the highest exposure levels are most likely to occur: small lakes and reservoirs

Acute concentrations of chlorpyrifos parent in flowing waters:

For set sampling intervals, maximum reported chlorpyrifos concentrations should be somewhat less than actual peak values, because of the typical failure of such samples to capture the maximum peaks associated with post-application runoff events. However, in cases where sampling is conducted at least once a week during the application season, EFED recommends using the maximum reported chlorpyrifos concentration in filtered samples of flowing surface water collected from streams and rivers of all sizes in 20 NAWQA study units over the last several years; $0.4 \mu\text{g L}^{-1}$ (Table 8), as an upper-bound estimate of the highest 96-hour concentration the majority of the U.S. population could be exposed to from flowing surface water. It is possible that more intense use of chlorpyrifos occurs in some runoff-prone areas not sampled in the NAWQA program, resulting in higher acute concentrations. Acute exposure levels are particularly likely to be high for those deriving their drinking water from smaller streams draining watersheds with more intense chlorpyrifos use.

It is probably more reasonable to use the maximum monitoring value than to use the conservative PRZM/EXAMS generated maximum peak EEC of $31 \mu\text{g L}^{-1}$ (Table 5) for a pond draining an adjacent 100% treated field (it is highly unlikely that anywhere near 100% of a watershed constituting a major drinking water source would be treated with chlorpyrifos in a given year.) We have calculated that, if chlorpyrifos use occurred at typical rates over the entire acreage of a major watershed (a highly unlikely scenario), then the chlorpyrifos concentration in a river draining this watershed could reach $16 \mu\text{g L}^{-1}$ (based upon back-calculations of actual monitoring data, see the section entitled "Conclusions on likely Drinking Water Exposure Levels" for further details).

Finally, it should also be noted that single chemical assessments probably underestimate risks by not taking into account possible additive or even synergistic effects with other pesticides having comparable toxicological modes of action.

Chronic concentrations of chlorpyrifos parent in flowing waters:

Our overall conclusion from this analysis by three methods is that the available monitoring data imply that chlorpyrifos chronic concentrations are unlikely to exceed $0.1 \mu\text{g L}^{-1}$ (the highest 90-day exposure level we confirmed to date was $0.06 \mu\text{g L}^{-1}$). However, since it is not clear if the monitoring data cover the most vulnerable watersheds and because modeling indicates exposure at higher levels in more vulnerable streams in higher-use watersheds is at least a plausible hypothesis, we recommend maintaining the upper-bound estimate for chronic exposure to chlorpyrifos in flowing surface waters at $0.4 \mu\text{g L}^{-1}$ (see the section entitled "Conclusions on likely Drinking Water Exposure Levels" for further details).

Acute and chronic concentrations of TCP in flowing waters:

No surface water monitoring data are available for the degradate TCP (3,5,6-trichloro-2-pyridinol), and currently no modeling methods for estimating pesticide residues in flowing waters have been adopted or developed by EPA. Consequently an estimation range rather than a single value was given for exposure to TCP in vulnerable areas.

Based on the high mobility and environmental persistence of TCP relative to chlorpyrifos parent, concentrations of TCP in surface waters are likely to be much higher than chlorpyrifos *per se*. The maximum modeled concentrations are $404 \mu\text{g L}^{-1}$ (acute, 4-day) and $304 \mu\text{g L}^{-1}$ (chronic, 60-day) for the sweet corn use, we used these values as the upper limit on our estimates of TCP concentrations in flowing waters. These values are likely to overestimate actual exposure because sweet corn represents a small use nationally, and all of the other uses are unlikely to occur over all or most of the watershed area in a given year as assumed by the model. Modeling results were consistent with the theory that TCP residues in surface waters are likely to be much higher from a given use than chlorpyrifos because of the much higher solubility, higher partitioning in water, and greater persistence of TCP compared to chlorpyrifos. We set a lower limit on TCP estimates by extrapolation of the modeled ratios of TCP in GENEED ponds to the chlorpyrifos flowing water measured concentrations (see later in this document for detail). This resulted in a range of 4.6 to $304 \mu\text{g L}^{-1}$ for chronic exposure and a range of 4.6 to $404 \mu\text{g L}^{-1}$ for acute exposure. Specific estimates are not feasible without actual monitoring data for TCP associated with chlorpyrifos use.

Part 4: Surface Water Exposure Levels - Lakes and Reservoirs.

We currently have no significant data on chlorpyrifos residues in reservoirs and lakes. Tier II Modeling values for a one hectare by two meter deep pond or lake surrounded by a completely chlorpyrifos-treated 10 hectare drainage basin ranged up to 31 (acute) and 6.7 (chronic) $\mu\text{g L}^{-1}$ for chlorpyrifos parent and 404 (acute) and 304 (chronic) for TCP. We have, in the absence of directly supportive monitoring data (no data at all for TCP), given a range of exposures for chlorpyrifos parent (**0.4 to 31 $\mu\text{g L}^{-1}$** for acute and **0.4 to 6.7 $\mu\text{g L}^{-1}$** for chronic exposure) and TCP (**4.6 to 404 $\mu\text{g L}^{-1}$** for acute and **4.6 to 304 $\mu\text{g L}^{-1}$** for chronic exposure) with the lower values in the exposure range based on extrapolated monitoring data and the higher values based on the highest Tier II modeled values for chlorpyrifos and Tier I modeled values for TCP. We believe actual exposures in vulnerable areas will be well below the high end of this range primarily because it is unlikely that chlorpyrifos usage in a watershed will be as pervasive as assumed in the modeling scenarios.

Maximum reported (and presumably actual peak) pesticide concentrations are typically less in reservoirs than in flowing water. However, peak multi-month or annual average concentrations are typically somewhat higher in reservoirs than in flowing water. Nevertheless, multi-month or annual mean concentrations in a reservoir should be less than the maximum reported concentrations in the flowing water feeding the reservoir. For this reason, we believe that high exposure levels for chlorpyrifos in reservoirs and lakes are more likely to be near 0.4 $\mu\text{g L}^{-1}$ (a high acute exposure level for streams) than the much higher modeled values. We have less confidence in saying this for TCP because of the total lack of monitoring data for TCP.

Environmental Fate Background for Drinking Water Assessment

The environmental fate data for chlorpyrifos and its major degradate 3,5,6-trichloro-2-pyridinol (TCP) used in the screening assessments are summarized in Tables 1 and 2. The persistence of chlorpyrifos parent and TCP have been found to be quite variable in different soils, but TCP tends to be significantly more persistent in many soils, and was particularly persistent under anaerobic conditions (Table 2). Unlike parent chlorpyrifos, TCP has the potential to be quite mobile in many soils, with the measured sorption coefficients in all soils studied being less than 2 ml/g.

There are two particularly important issues with regard to chlorpyrifos use that greatly affect the degree to which the parent compound impacts water resources and potentially impacts drinking water quality (issues with regard to the degradate, TCP, are discussed further below):

- (1.) Application rate and method, with much higher residues in ground water used for drinking associated with termiticidal uses around dwellings (at much higher rates and much more deeply incorporated than agricultural uses); and
- (2.) Soil persistence, which appears to vary over about two orders of magnitude (from a few days to well over 100 days and typically greater than 200 days for termiticidal uses) depending on soil type, environmental conditions, and possibly previous use history at the treatment site (Tables 1, 2, and 3).

TABLE 1. Summary of Selected Environmental Fate Properties for Chlorpyrifos.

Property	Range (mean or median)	Value used in assessment	Model
Solubility	2.0 mg/L (ppm)	2.0 mg/L (ppm)	GENEEC, PRZM-EXAMS

Property	Range (mean or median)	Value used in assessment	Model
Hydrolysis	pH 5: 72 days pH 7: 72 days pH 9: 16 days	72 days	GENEEC, PRZM-EXAMS
Photolysis	30 days @ pH 7	29.6	GENEEC, PRZM-EXAMS
Aerobic Soil Metabolism $T_{1/2}$	11 to 180 days (mean = 63 days) ¹	180 days 76.9 days 63 days	GENEEC PRZM-EXAMS SCI-GROW
<i>Aerobic soil metabolism $t_{1/2}$, termiticide rates</i>	<i>175 to 1576 days (mean = 506 days) (median = 230 days)²</i>	<i>506 days</i>	<i>SCI-GROW</i>
Field dissipation $T_{1/2}$ (supporting information only)	1 to 56 days at 6 sites (mean = 27 days) ³	not directly used	---
Anaerobic Soil Metabolism $T_{1/2}$	39 to 51 days (2 soils)	not considered	---
Aerobic Aquatic Metabolism $T_{1/2}$	no data	0 days (no metabolism)	---
K_{ads}	50 to 260	not used	---
K_{oc}	360 to 31000	6070	GENEEC, PRZM-EXAMS/SCI-GROW

¹ The range of half-lives in a 1979 study with undisturbed samples from seven different soils was 11 to 141 days. The mean and median half-lives were 63 and 34 days, respectively. 180-day half-life measured in a subsequent study of metabolism in one soil.

² Racke, K.D.; D.D. Fontaine, R.N. Yoder, J.R. Miller. 1994. Chlorpyrifos degradation in soil at termiticidal application rates. Pestic. Sci. 42:43-51. This published study was conducted by DowElanco, the registrant.

³ Half-lives or 50 % disappearance times in three sets of studies were:
33, 46, 56 days (3 sites) 1.3 to ~15 days (3 applic. at 1 citrus site), data too variable to estimate precisely 6 to 11 days at 2 sites with fallow & turf applications (longer secondary "half-lives").

TABLE 2. Summary of Selected Environmental Fate Properties for 3,5,6-trichloro-2-pyridinol.

Property	Range (mean or median)	Value used in assessment	Model
Solubility	117 mg/L (ppm) at pH 2.5, increases at higher pH	500 mg/L (ppm)	GENEEC
Hydrolysis	pH 5: >> 30 days ¹ pH 7: >> 30 days pH 9: >> 30 days	180 days	GENEEC, PRZM-EXAMS, SCI-GROW

Property	Range (mean or median)	Value used in assessment	Model
Photolysis	0.33 days (soil)	1 day	GENEEC, PRZM-EXAMS, SCI-GROW
Aerobic Soil Metabolism $T_{1/2}$	600 days estimated. range 65 to >360 in parent studies ²	600 days	GENEEC, PRZM-EXAMS, SCI-GROW
<i>Aerobic soil metabolism $t_{1/2}$, termiticide rates</i>	<i>>> 24 months in each of 5 soils</i>	<i>1500 days</i>	<i>SCI-GROW</i>
Anaerobic Soil Metabolism $T_{1/2}$	>500 and >1500 days (2 soils) ³	not considered	GENEEC, PRZM-EXAMS
Aerobic Aquatic Metabolism $T_{1/2}$	no data	0 days (no metabolism)	---
K_{ads}	0.53 to 1.95 ml/g; 0.3 to 20.3 in previous study. ⁵	not used	---
K_{oc}	77 to 242 (136, geometric mean); 27 to 389 (168 mean) in previous study. ³	136	GENEEC, PRZM-EXAMS, SCI-GROW

¹ TCP accumulated without apparent degradation over the 30-day study period at each pH.

² In seven soils, half-lives estimated to be (soil series name in parenthesis):

≤ 70 days (Commerce) ≤ 220 days (Barnes)
 ≥ 360 days (Norfolk) ≤ 65 days (Miami)
 ≤ 220 days (Catlin) ≤ 90 days (German)
 ≥ 360 days (Stockton)

These estimates are from the aerobic metabolism studies with chlorpyrifos parent applied.

³ Racke, K.D. and S.T. Robbins. 1991. Factors affecting the degradation of 3,5,6-trichloro-2-pyridinol in soil. Amer. Chem. Soc., Symposium Series No. 459, pp. 93-107.

25 soils were tested in this study, however, desorption coefficients were not determined.

Table 3. Variation of chlorpyrifos persistence in two soils at different application rates (initial soil concentrations from 10 to 1000 ppm) and at different temperatures and soil moisture levels (Racke, K.D.; D.D. Fontaine, R.N. Yoder, and J.R. Miller. 1994. Chlorpyrifos degradation in soil at termiticidal application rates. Pestic. Sci. 42:43-51.)

Applic. Rate, µg L ⁻¹	State	15 C, medium water	15 C, high water	25 C, medium water	25 C high water	35 C medium water	35 C high water
Half-life in months							
10	Texas	<1	<1	<1	<1	<1	<1
10	Florida	>24	15	115	4	5	3
100	Texas	4	3	1	1	<1	<1
100	Florida	>24	22	15	3	6	4
1000	Texas	6	30	10	6	2	3
1000	Florida	>24	>24	>24	>24	11	11

Use Characterization

Chlorpyrifos has significant usage for both agricultural and non-agricultural sites (Table 4 summarizes selected usage estimates from BEAD and other sources).

TABLE 4. Summary of chlorpyrifos usage.¹

Use Site	BEAD, 1993	DowElanco, 1993	USDA, 1995 or 1996	NCFAP, 1997
Total Agricultural	12,250	16,150	---	---
-- Corn	6,700	---	5,877	7,141
-- Alfalfa	640	---	---	1,074
-- Apples	>200	---	593	657
-- Oranges	>200	---	578	695
Total non-agricultural	10,175	8,977	---	---
-- Termiticide	7,123	6,330	---	---
-- Retail products	1,470	---	---	---

¹BEAD = Biological & Economic Analysis Division, EPA

USDA = U.S. Dept. of Agriculture, National Agricultural Statistics Service

NCFAP = National Center for Food and Agricultural Policy, use estimates were in acres treated, data were converted to total pounds applied per year from other data on pounds applied per year per treated acre for each crop.

Recently, the Biological and Economic Analysis Division (BEAD) of the Office of Pesticide Programs has estimated that more than 22,000,000 lbs active ingredient are used yearly, slightly more being used in agriculture (12,250,000 lbs ai) than non-agriculture (10,175,000 lbs ai)+. The largest single type of use is for control of termites around dwellings (BEAD estimate of 7,123,000 pounds ai annually). Confirmation for the significance of

this use is provided by a recent survey of Certified Commercial Pesticide Applicators for non-agricultural uses¹, which estimated that certified applicators in the United States in 1993 applied 7,779,000 pounds of chlorpyrifos for non-agricultural purposes; of this amount 5,065,000 pounds was estimated to be used for termite control (3,634,000 pounds applied outdoors and 1,431,000 pounds applied indoors).

The two highest crop uses are corn (6,700,000 lbs ai -- 55% of the total agriculture volume is applied to 8% of the planted corn acreage) and alfalfa (640,000 lbs ai -- 5% of the total agriculture volume is applied to 4% of the planted acreage). Other crops with chlorpyrifos usage over 200,000 lbs ai include almonds, apples, cotton, oranges, peanuts, pecans, sorghum, soybeans, sugar beets, tobacco, walnuts and wheat. Crops with more than 50% of planted acreage treated with chlorpyrifos include apples, Brussels sprouts, cauliflower, oranges, sweet potatoes, and walnuts. The highest use states in descending order are California, Washington, Georgia, Florida, Arizona, Nebraska, Iowa, Illinois, and Wisconsin.

Registered non-crop uses of chlorpyrifos include termiticide, turf, golf courses, cattle ear tags, turkey farms, ULV mosquito adulticide, ornamental sites, indoor pest control, and pet tick and flea products, etc.). Approximately 70% of non-agricultural use of chlorpyrifos is used for control of subterranean termites. About 14% of non-agricultural use is retail, such as pet collars, baits, dusts, aerosols, ear tags, pet shampoos, pet dips and paint additives. Other major non-agricultural uses include golf courses and turf (7%), indoor (5%), residential perimeter treatments (3%), and ornamentals (1%).

The termiticide applications are made by professional applicators; an average application rate for the termiticide is 10.25 lb/structure as a soil application, either by trenching, rodding, or injection. The rodding treatment involves injection of the chlorpyrifos solution/suspension into the soil through a hollow metal rod (usually about four feet in length). This may allow chlorpyrifos to contaminate aquifers at relatively very high concentrations because of direct entry into subsurface macropores (cracks, root channels, etc.) that connect with the ground water (see the "Drinking Water Assessment" section later in this chapter).

For surface water screening, the current GENEEC and PRZM-EXAMS modeling procedures do not provide adjustments for actual use intensities in watersheds (only a few percent of the acres are treated with chlorpyrifos in most watersheds across the country since only relatively small-acreage crops have a high percent crop-treated factor for this insecticide) and do not include scenarios representing larger lakes or reservoirs or riverine drinking water sources. These limitations may result in significant overestimates of impacts because of large overestimates in use. As an example of this, take the White River, Indiana Basin study in the U.S. Geological Survey's National Water Quality Assessment program (detailed data are not yet available for other NAWQA study units). Some of the highest detection levels to date for chlorpyrifos in the NAWQA program have been in the White River Basin study. Chlorpyrifos is estimated to be applied in this basin on only about 1 to 3% of the watershed acreage (agricultural usage estimates, Table 5) at rates averaging substantially less than the label maximums. This analysis demonstrates that, at least for most larger watersheds commonly associated with drinking water sources, modeling assumptions of 100% of the watershed being treated dramatically overestimate actual treatment rates. However, it cannot be ruled out that the proportion of watershed acres treated could be much higher for some smaller watersheds in some parts of the United States. For example, chlorpyrifos is estimated to be used on more than 50% of orange or apple acres each year. On citrus, which is a major crop in some counties in Florida and California, applications may be up to 7.5 lbs ai./year. If further refinement of drinking water exposure level estimates is needed, then further geographic analysis of cropping patterns and usage patterns is needed to identify counties or other local areas where chlorpyrifos usage is likely to be most intense.

Lucas, Robert M.; Kerrie E. Boyle, Jill A. Dever, Barbara J. George, and Christy J. Jeffries. 1995. FINAL REPORT _ VOLUME 1 RESULTS OF THE 1993 CERTIFIED/COMMERCIAL PESTICIDE APPLICATOR SURVEY. EPA Contract Number: 68D20169. Research Triangle Institute, Research Triangle Park, NC. RTI Project No: 6012-080.

TABLE 5. Example of agricultural use intensity and trends in a monitoring study area with high detections of chlorpyrifos in Surface water (White River Basin Study, USGS NAWQA program. This watershed covers most of southern Indiana. Detailed data are given for usage on corn, the dominant use of chlorpyrifos in this watershed).

Year	% Corn Crop Treated:	Pounds applied on corn statewide*	Typical use rate (lbs./ acre/ year on corn)	% of Watershed Treated, all agricultural uses [#] (corn in parenthesis)
1992	8	574,000	1.14	2.61 (1.76)
1993	6	374,000	1.04	2.11 (1.25)
1994	7	470,000	1.14	2.38 (1.44)
1995	4	249,000	1.14	1.52 (0.76)
1996	11	730,000	1.18	3.32 (2.16)

* Estimates of Anderson and Gianessi (1995) are that an average of about 30% of this usage statewide occurred in the White River Basin.

[#] Includes only agricultural uses (agriculture is the dominant land use in the White River basin, crop acreage constitutes about 50% of the basin land area each year, and about 40% of the basin planted to corn or soybeans each year). Basin estimates of chlorpyrifos treatment for each year were based on data from Crawford et al. (1996), USDA-NASS (1993, 1994, 1995, and 1996) and the Center for Food and Agricultural Policy (1996). Some imputation for non-row crop usage data was required, but statewide and/or state region estimates of chlorpyrifos usage on row crops were available for each year.

Detailed Drinking Water Assessment:

Because the impacts on water resources from the termiticidal uses of chlorpyrifos are more localized but also potentially much more intense, termiticidal uses are discussed in a separate section of this Drinking Water Assessment.

Part I: Agricultural and other Non-termiticidal Uses

Modeling Results:

Estimates of chlorpyrifos and TCP concentrations that might occur in highly vulnerable ground waters and surface waters are given in Table 6 for four different use scenarios (additional PRZM-EXAMS scenarios for chlorpyrifos parent in surface waters are given in the EFED RED chapter). Modeling was done with the GENEEC and SCI-GROW models for TCP and chlorpyrifos. Higher tier PRZM-EXAMS scenarios are also included for chlorpyrifos parent.

Ground-Water Summary: Modeling results highlight the relatively low potential of chlorpyrifos parent to leach to ground water from agricultural uses (concentrations of $0.1 \mu\text{g L}^{-1}$ or less in highly vulnerable ground water) but very high potential for the TCP degradate to leach (up to $85 \mu\text{g L}^{-1}$ in ground water).

Ground-water modeling results were obtained with the SCI-GROW model, which uses actual monitoring data for various pesticides at sites with sandy soils and vulnerable ground water to facilitate estimation of concentrations of other pesticides that may occur in similarly vulnerable ground water. The estimates derived with SCI-GROW are based on the high 90-day concentrations observed in shallow ground water for a set of reference compounds. These concentrations serve as both chronic and acute exposure estimates at the current time because of the difficulty in separating out seasonal differences in ground water. Concentrations would be expected to be significantly lower in the majority of the use area for chlorpyrifos where ground water is not as vulnerable to

contamination.

Surface Water Summary: Modeling estimates for surface water concentrations of chlorpyrifos parent are relatively high, especially for acute exposure. To represent chronic exposure, the highest Tier 1 60-day estimated surface water concentrations (EECs) were 15 and 304 $\mu\text{g L}^{-1}$ for chlorpyrifos and TCP, respectively (Tier II estimate for chlorpyrifos parent was 6.7 $\mu\text{g L}^{-1}$ for a 90-day exposure). To represent acute exposure, the highest Tier I 4-day EECs were 50 and 404 $\mu\text{g L}^{-1}$ for chlorpyrifos and TCP, respectively (the highest Tier II 4-day estimate for chlorpyrifos was 31 $\mu\text{g L}^{-1}$).

TABLE 6. Estimated environmental concentrations of chlorpyrifos and its degradate TCP in vulnerable surface and ground waters. Surface water estimates made with GENEEC or PRZM-EXAMS as noted; ground water estimates made with SCI-GROW.

Part I: Tier II Assessments (available for chlorpyrifos parent in surface waters only).

Site, Application method (runoff model used)	Appl. Rate ¹ (lbs ai /A)*	Pond Water					Shallow ground water
		Initial (PEAK) EEC ($\mu\text{g L}^{-1}$)	4-Day average EEC ($\mu\text{g L}^{-1}$)	21-day average EEC ($\mu\text{g L}^{-1}$)	60-day average EEC ($\mu\text{g L}^{-1}$)	90-day average EEC ($\mu\text{g L}^{-1}$)	Ground-water screen. conc., ($\mu\text{g L}^{-1}$)
Citrus - Florida (PRZM-EXAMS) Adamsville Sand, airblast 30-day interval	2 x 3.5 (Cp)	27.6	21.4	11.8	8.3	6.7	---
Corn - Iowa (PRZM-EXAMS) Marshall Silty Clay Loam, 1 ground spray appl., incorp. 2"	1 x 3 (Cp)	11.1	8.7	4.5	2.7	1.9	
Sweet corn - GA spray (PRZM-EXAMS) Cowarts Sandy Loam	11 x 1.0 (Cp)	15.8	12.8	7.4	5.6	4.3	---
Tobacco - NC (PRZM-EXAMS) Norfolk Loamy Sand, ground.	1 x 5 (Cp)	40.6	31	14.7	7.7	5.4	---

¹ Number of applications x the lb ai/A rate for each application. For the degradate immediate 100% conversion was assumed. Cp = chlorpyrifos parent, TCP = 3,5,6-trichloro-2-pyridinol degradate. TCP residue estimates are given in italics.

TABLE 6, Part II. Tier 1 Surface Water and Ground Water Assessments for 3,5,6-trichloro-2-pyridinol and chlorpyrifos (the Surface Water Tier 2 values in Part I above should be used for exposure assessment for

chlorpyrifos parent).

		Pond Water					Shallow ground water
Site, Application method (runoff model used)	Appl. Rate ¹ (lbs ai /A)*	Initial (PEAK) EEC (µg L ⁻¹)	4-Day average EEC (µg L ⁻¹)	21-day average EEC (µg L ⁻¹)	60-day average EEC (µg L ⁻¹)	90-day average EEC (µg L ⁻¹) ¹	Ground-water screen. conc., (µg L ⁻¹)
Corn - foliar spray (GENEEC) broadcast	1 x 1.5 (Cp)	5.5	4.8	2.6	1.5	---	0.015
	1 x 1.5 (TCP)	<i>56.3</i> (TCP)	<i>55.3</i> (TCP)	<i>50.1</i> (TCP)	<i>41.6</i> (TCP)	---	<i>11.7</i> (TCP)
Sweet corn - foliar spray (GENEEC)	11 x 1.0 (Cp)	56.5	49.9	26.3	14.5	---	0.111
Sweet corn - foliar spray (GENEEC)	11 x 1.0 (TCP)	<i>411.4</i> (TCP)	<i>404.2</i> (TCP)	<i>366.2</i> (TCP)	<i>304.3</i> (TCP)	---	<i>85.7</i> (TCP)
Citrus - aerial (GENEEC) 30-day interval	2 x 3.5 (Cp)	36.1	31.9	16.8	9.3	---	0.071
Citrus - aerial (GENEEC) 30-day interval	2 x 3.5 (TCP)	<i>261.9</i> (TCP)	<i>257.3</i> (TCP)	<i>233.2</i> (TCP)	<i>193.8</i> (TCP)	---	<i>54.5</i> (TCP)
Tobacco - ground spray (GENEEC)	1 x 5 (Cp)	18.4	15.9	8.7	5.0	---	0.051
Tobacco - ground spray (GENEEC)	1 x 5 (TCP)	<i>187.7</i> (TCP)	<i>184.4</i> (TCP)	<i>167.0</i> (TCP)	<i>138.8</i> (TCP)	---	<i>38.9</i> (TCP)

¹ Number of applications x the lb ai/A rate for each application. For the degradate immediate 100% conversion was assumed. Cp = chlorpyrifos parent, TCP = 3,5,6-trichloro-2-pyridinol degradate. TCP residue estimates are given in italics.

Monitoring Results

Ground-Water Monitoring. Based on information from environmental fate studies, chlorpyrifos parent is unlikely to leach to ground water in measurable quantities from most typical use scenarios (the termiticide use, for which ground-water monitoring data are discussed below, represents an important exception). In two terrestrial field dissipation studies (**40059001** and **40395201**), chlorpyrifos was not detected at soil depths greater than 18 inches at any time during the studies. Widespread monitoring data indicate that some low-level contamination (usually below 0.01 µg L⁻¹) of ground-water with chlorpyrifos parent may result from agricultural or urban uses (Table 7).

TABLE 7. Summary of chlorpyrifos residue distributions in major ground-water monitoring studies for chlorpyrifos.

Study Identification	Location, type of ground water	Number of samples or sites	Detection limit, $\mu\text{g L}^{-1}$	% Detections	90th percentile conc.	95th percentile conc	Highest Detection
Gilliom et al. (1998, USGS web site)	20 NAWQA study units all over U.S.: Shallow g.w., agric. areas	1130	0.004	0.26	<0.004	<0.004	0.006
Gilliom et al. (1998, USGS web site)	20 NAWQA study units all over U.S.: shallow urban wells	330	0.004	0.30	<0.004	<0.004	0.036
Gilliom et al. (1998, USGS web site)	20 NAWQA study units all over U.S.: major aquifers	1089	0.004	0.09	<0.004	<0.004	0.013
Jacoby et al. (1992, PGWDB)	CA, FL, HI, IA, IL, IN, MA, ME, MS, MN, MO, NE, NH, NY, OK, OR, PA, TX, VA	5398	variable	0.59	no data	no data	0.654

Only one study is known to be available which includes analysis for chlorpyrifos degradates in ground water. In a well-water monitoring study conducted on a sand soil, chlorpyrifos and its degradates, TCP and 2-methoxy-3,5,6-trichloropyridine (MOTCP), were not detected (detection limits $0.250 \mu\text{g L}^{-1}$, $50.00 \mu\text{g L}^{-1}$, and $10.00 \mu\text{g L}^{-1}$, respectively) at any sampling interval in the water from two wells located in an orange grove in Highlands County, Florida that received three, 1 lb ai/A applications of chlorpyrifos (**MRID 40059001**). This study is not particularly enlightening, however, on the leaching potential of the degradates because of the relatively very high minimum reporting levels for these compounds. In fact, reports of any pesticide residue in ground-water at concentrations exceeding $50 \mu\text{g L}^{-1}$ (the minimum reporting limit for the degradate TCP) from agricultural applications are **extremely rare** except for a few compounds applied at higher rates. If TCP had occurred at $49 \mu\text{g L}^{-1}$ in a ground-water sample, it would not have been reported in this study. Unless it can be determined that no adverse impacts of TCP on drinking water quality can arise from concentrations well in excess of $50 \mu\text{g L}^{-1}$, this study provides no useful information on chlorpyrifos degradates in drinking water. Assumption that vulnerable ground water used for drinking water may be contaminated with TCP at a level of up to $50 \mu\text{g L}^{-1}$ seems reasonable given that the SCI-GROW screening concentration for the citrus use is $54.5 \mu\text{g L}^{-1}$ for TCP and that citrus is commonly grown in areas with sandy soils and vulnerable ground water.

Surface-Water Monitoring. For chlorpyrifos parent the available surface water monitoring shows dissolved

residues tend to be higher and more frequently detected in surface waters than in ground water, but still are no more than a fraction of a part per billion in a large variety of streams and rivers from all over the United States (Tables 8 and 9). These concentrations are much less than the EECs for pond scenarios with the GENEEC and PRZM-EXAMS models (ranging up to 50 µg/L for a 4-day period, for example). Although it is likely that the EECs from these model runs overestimate concentrations that occur in streams and reservoirs, the amount of the overestimate in small reservoirs (shown to have the highest time-weighted mean concentrations for moderately to highly persistent pesticides) cannot be determined because of the lack of monitoring data for reservoirs.

All of these monitoring residue data represent dissolved chlorpyrifos, there are often significant additional residues of this lipophilic pesticide in sediment and suspended solids. Therefore, these estimates apply only to drinking water exposure potential.

No surface water monitoring data are available for TCP.

TABLE 8. Summary results of major surface water monitoring studies for chlorpyrifos parent (residues are explicitly stated to be, or appear to be, for dissolved residues in these studies).

Study Identification	Location, type of water	Number of samples or sites	Detection limit, µg L ⁻¹	% Detections	Highest Detection
Wnuk et al. (1987)	Iowa, community water supply systems	35 sites	0.1	0.0	<0.1
Moyer and Cross (1990)	Illinois	30 sites	0.05	0.0	<0.05
Goolsby and Battaglin (1993)	Mississippi River basin rivers and streams	381 samples, 8 sites	0.005	3.1	0.2
Kimbrough and Litke (1995)	two Colorado watersheds	50 samples, 2 watersheds	0.008	12.0	0.08
MacCoy et al. (1995) (samples collected every day or two from one location)	San Joaquin River, CA	~200 samples, 1 location	0.012	~6	0.04
Gilliom et al. (1997, USGS web site)	20 NAWQA study units all over U.S.: agricultural streams	1530 samples, 37 streams	0.010	14.6	0.40
Gilliom et al. (1997, USGS web site)	20 NAWQA study units all over U.S.: urban streams	604 samples, 11 streams	0.010	26.5	0.19
Gilliom et al. (1997, USGS web site)	20 NAWQA study units all over U.S.: mixed-land use large streams	555 samples, 14 streams	0.010	14.4	0.13

Study Identification	Location, type of water	Number of samples or sites	Detection limit, $\mu\text{g L}^{-1}$	% Detections	Highest Detection
Hippe et al. (1994, USGS Report 94-4183)	Apalachicola-Chattahoochee-Flint Rivers, GA, AL, FL	57 weekly samples, Urban watershed	~0.005	65.0	0.051
Crawford et al. (1995, USGS Fact Sheet 233-95, USGS web site, and personal communication)	White River Basin, southern Indiana.	585 samples, 6 streams and rivers	0.004	27.7	0.130
Thurman et al. (1998, USGS Fact sheet FS-022-98)	Mississippi delta: cotton production areas of LA, MS, AR, TN, KY, & MO.	64 sites in streams and rivers	0.010	2	0.2

TABLE 9. Distributional analysis of dissolved chlorpyrifos residues in large-scale surface-water monitoring studies.

Study Identification	Location, type of water	Number of samples or sites	Detection limit, $\mu\text{g L}^{-1}$	% Detections	90th Percentile Detection	95th Percentile Detection	Highest Detection
Gilliom et al. (1997, USGS web site)	20 NAWQA study units all over U.S.: agricultural streams	1530 samples, 37 streams	0.010	14.6	0.017	0.031	0.400
Gilliom et al. (1997, USGS web site)	20 NAWQA study units all over U.S.: urban streams	604 samples, 11 streams	0.010	26.5	0.020	0.038	0.190
Gilliom et al. (1997, USGS web site)	20 NAWQA study units all over U.S.: mixed-land use large streams	555 samples, 14 streams	0.010	14.4	0.012	0.020	0.130

Study Identification	Location, type of water	Number of samples or sites	Detection limit, $\mu\text{g L}^{-1}$	% Detections	90th Percentile Detection	95th Percentile Detection	Highest Detection
Crawford et al. (1995, USGS Fact Sheet 233-95, USGS web site, and personal communication)	White River Basin, southern Indiana. Data collected from 1992 to 1996.	585 samples, 6 streams and rivers	0.004	~14	0.016	0.025	0.130

Conclusions on Likely Drinking Water Exposure Levels (non-termiticidal uses)

1. Ground-Water Sources.

Acute and Chronic Exposure. Although the available monitoring data chlorpyrifos represent a large part of the United States, it is not clear that they represent the most vulnerable ground and surface waters where chlorpyrifos is used most intensely in the United States. The largest detection in about 3000 NAWQA wells across the country has been $<0.04 \mu\text{g L}^{-1}$ (Table 7). The Pesticides in Ground Water Database has a maximum reported value of $0.65 \mu\text{g L}^{-1}$. These compare with a SCI-GROW ground-water screening concentration of $0.11 \mu\text{g L}^{-1}$ for the sweet corn use. Given the large weight of support of the NAWQA data for the SCI-GROW value being sufficiently conservative, it is reasonable to conclude that the large majority of the country ($> 99\%$) will not have ground-water usable for drinking water contaminated with chlorpyrifos parent at levels exceeding $0.1 \mu\text{g L}^{-1}$.

For TCP, in the absence of usable monitoring data, we estimate the most vulnerable ground water usable for drinking water may be contaminated with this compound at a level of about $85.7 \mu\text{g L}^{-1}$ (the SCI-GROW value for the sweet corn use).

2. Surface Water Sources - Flowing Waters.

Acute Exposure to Chlorpyrifos. For set sampling intervals, maximum reported chlorpyrifos concentrations should generally be somewhat less than actual peak values, because of the typical failure of such samples to capture the maximum peaks associated with post-application runoff events. However, in cases where sampling is conducted at least once a week during the application season, EFED recommends using the maximum reported chlorpyrifos concentration in filtered samples of flowing surface water collected from 20 NAWQA study units over the last several years of $0.4 \mu\text{g L}^{-1}$ (Tables 8 and 9) as a high estimate of the typical concentration for acute drinking water assessments for flowing surface water. The reason is that it is probably more reasonable than using the conservative PRZM/EXAMS generated maximum peak EEC of $31 \mu\text{g L}^{-1}$ (Table 6) for a pond draining an adjacent 100% treated field (it is highly unlikely that anywhere near 100% of a watershed constituting a major drinking water source would be treated with chlorpyrifos in a given year.) We are also recommending that the $0.4 \mu\text{g L}^{-1}$ be used for the time being for chronic exposure, although this is more conservative as an estimate of chronic exposure (see the analysis below).

We caveat our estimates with the notation that there may be a limited number of watersheds across the U.S. where the usage rate of chlorpyrifos is higher and/or the pesticide runoff likelihood is greater than in any of the watersheds for which we have multi-year monitoring data to date. Acute exposure levels are particularly likely be high for those deriving their drinking water from streams draining watersheds with more intense chlorpyrifos use.

What about acute concentrations of chlorpyrifos in rivers or major streams in watersheds that might have higher use intensities of chlorpyrifos than those sampled to date? We have analyzed a specific data to provide some perspective on the data (this analysis was not directly used in the quantitative exposure assessment): For surface water, although widespread monitoring data in streams and rivers are available, we are still uncertain whether any relatively small watersheds which might have much more intense use of chlorpyrifos, have been sampled. Consequently, based on our analysis of usage in one of the major study units with significant chlorpyrifos use (White River Basin, see Table 5) we divided the highest detection in these studies ($0.4 \mu\text{g L}^{-1}$) by 0.025 (the average chlorpyrifos treated acre proportion for the five years in Table 5) to get $16 \mu\text{g L}^{-1}$ as an upper bound estimate of acute exposure (I.e., 100% treatment of the acreage in a specific watershed with high runoff potential could be 40 times higher than in the watersheds for which streams have been sampled so far). Note that if, for example, the maximum chlorpyrifos-usage rate for any major U.S. watershed was 10% of the treated acreage at similar per acre rates (much more likely than 100%), then this upper bound estimate for acute exposure drops to $1.6 \mu\text{g L}^{-1}$. On the other hand, this procedure may underestimate the concentrations of chlorpyrifos that may occur under more intense usage scenarios because the attenuation of residues could be less significant as the travel times and distances for residues entering streams may be reduced with more intense usage.

Collection of additional monitoring data targeted to high-use watersheds for chlorpyrifos or analysis of additional geographically-specific chlorpyrifos usage data would facilitate a more refined estimate of this value.

Chronic Exposure to Chlorpyrifos. Specific calculation of longer-term exposure levels is not directly possible from most of the data currently available (individual sample data and sample attribute information are generally not available). For flowing waters, we have made some approximate calculations from the NAWQA summary data that are available and have also made some specific calculations using the White River Basin NAWQA study unit data, for which we do have sample-by-sample reports.

1. Method 1: Specific Calculations of Concentrations in Rivers Using the White River Data set (this method can be applied to numerous streams and rivers across the country from the other NAWQA studies as the data become available).

Although it appears that this basin tends to have one of the highest chlorpyrifos loadings of the USGS study units, insufficient information are available to determine which watersheds in these study areas may tend to have more chlorpyrifos use and/or more of the applied chlorpyrifos lost to surface runoff. Table 10 shows the highest 2- or 3-month concentrations for chlorpyrifos for each of three years in which significant runoff was detected. The highest chronic exposure value was **$0.061 \mu\text{g L}^{-1}$** . This watershed had major agricultural and non-agricultural usages (termiticide use, for example, is approximately proportional to the human population, which was about 2.1 million in 1990 in the White River Basin) and the watershed has some soils particularly prone to runoff (Charlie Crawford, USGS, Indianapolis, IN; personal communication), so it is not expected that residues in other major rivers in other parts of the country would commonly be significantly higher than in the White River.

Dividing the highest chronic exposure value ($0.061 \mu\text{g L}^{-1}$) by 0.025 (as above), gives an estimate of $2.4 \mu\text{g L}^{-1}$ of chlorpyrifos in the Hazelton River over two or three months if chlorpyrifos was applied at similar rates over 100% of the watershed (residues could be higher if the high use resulted in less opportunity for retention of residues in the soil before runoff to streams occurred). Note that the maximum single-sample detection level for chlorpyrifos for all samples from all study units to date is $0.4 \mu\text{g L}^{-1}$.

It is also interesting to compare these calculated values to GENEEC modeling results for field corn (bear in mind that GENEEC is suppose to estimate concentrations in a pond rather than a river), which is by far the dominant agricultural use of chlorpyrifos in the White River basin. The highest 60-day concentration estimated with GENEEC was $1.5 \mu\text{g L}^{-1}$ for field corn, about 25 to 75x greater than the actual highest 60- or 90-day concentrations in the White River. However, the modeled value of $1.5 \mu\text{g L}^{-1}$ is actually somewhat less than what would be expected in a river from the monitoring data if the entire watershed was planted to corn and treated with

chlorpyrifos (at least $2.4 \mu\text{g L}^{-1}$), even though the river has more rapid turnover of water than does the pond.

3. Method 2: GENEEC and PRZM-EXAMS Estimates of Small Lake or Pond Concentrations.

As discussed above, modeling estimates (which are suppose to represent a pond or small lake where the entire watershed has been treated) were much higher than actual river residues and somewhat higher than the river residues adjusted for an assumption of 100% use. The highest Tier II modeling EECs were $8.3 \mu\text{g L}^{-1}$ for 60 days and $6.7 \mu\text{g L}^{-1}$ for 90 days (from PRZM-EXAMS modeling of citrus). If only 10% of a watershed were treated at similar rates with chlorpyrifos, then this estimate would drop to $0.67 \mu\text{g L}^{-1}$.

Our overall conclusion from this analysis by two methods is that the available monitoring data imply that chlorpyrifos chronic concentrations are highly unlikely to exceed $0.1 \mu\text{g L}^{-1}$ (residues very rarely exceeded this level at any NAWQA study site). However, since it is not clear if the monitoring data cover the most vulnerable watersheds and because modeling indicates exposure at higher levels in more vulnerable streams in higher-use watersheds is at least a plausible hypothesis, we recommend maintaining at the current time the upper-bound estimate for chronic exposure to chlorpyrifos in flowing surface waters at $0.4 \mu\text{g L}^{-1}$.

TABLE 10. Seasonal high concentrations of chlorpyrifos in the White River near Hazelton (highest 2- or 3-month selected, concentrations in 1992 and 1994 were lower) (Source: Charles Crawford, U.S. Geological Survey, Indianapolis, IN).

Year	# of Days of Exposure	Time-weighted mean, $\mu\text{g L}^{-1}$	Flow/time weighted mean, $\mu\text{g L}^{-1}$
1993	63	0.020	0.023
1995	96	0.030	0.047
1996	68	0.059	0.061

Acute and chronic concentrations of TCP in flowing waters. No surface water monitoring data are available for the degradate TCP (3,5,6-trichloro-2-pyridinol), and currently no modeling methods for estimating pesticide residues in flowing waters have been adopted or developed by EPA. Consequently an estimation range rather than a single value was given for exposure to TCP in vulnerable areas.

Based on the high mobility and environmental persistence of TCP relative to chlorpyrifos parent, concentrations of TCP in surface waters are likely to be much higher than chlorpyrifos *per se*. The maximum modeled concentrations are $404 \mu\text{g L}^{-1}$ (acute, 4-day) and $304 \mu\text{g L}^{-1}$ (chronic, 60-day) for the sweet corn use, we used these values as the upper limit on our estimates of TCP concentrations in flowing waters. These values are likely to overestimate actual exposure because sweet corn represents a small use nationally, and all of the other uses are unlikely to occur over all or most of the watershed area in a given year as assumed by the model. Modeling results were consistent with the theory that TCP residues in surface waters are likely to much higher from a given use than chlorpyrifos because of the much higher solubility, higher partitioning in water, and greater persistence of TCP compared to chlorpyrifos.

We set a lower limit on TCP estimates by extrapolation of the modeled ratios of TCP in GENEEC ponds to the chlorpyrifos flowing water measured concentrations. The lowest ratio observed was 11.5 for 4-day concentrations arising from the use on field corn. Since our estimates for acute exposure to chlorpyrifos was $0.4 \mu\text{g L}^{-1}$, this means a lower limit on our estimate for TCP would be 11.5×0.4 or $4.6 \mu\text{g}$. Adding in the Tier I modeling results

for TCP results in a range of 4.6 to 304 $\mu\text{g L}^{-1}$ for chronic exposure and a range of 4.6 to 404 $\mu\text{g L}^{-1}$ for acute exposure. Specific estimates are not feasible without actual monitoring data for TCP associated with chlorpyrifos use.

Surface Water Exposure Levels - Lakes and Reservoirs.

We currently have no significant data on chlorpyrifos residues in reservoirs and lakes. Tier II Modeling values for a one hectare by two meter deep pond or lake surrounded by a completely chlorpyrifos-treated 10 hectare drainage basin ranged up to 31 (acute) and 6.7 (chronic) $\mu\text{g L}^{-1}$ for chlorpyrifos parent and 404 (acute) and 304 (chronic) for TCP. We have, in the absence of directly supportive monitoring data (no data at all for TCP), given a range of exposures for chlorpyrifos parent (**0.4 to 31 $\mu\text{g L}^{-1}$** for acute and **0.4 to 6.7 $\mu\text{g L}^{-1}$** for chronic exposure) and TCP (**4.6 to 404 $\mu\text{g L}^{-1}$** for acute and **4.6 to 304 $\mu\text{g L}^{-1}$** for chronic exposure) with the lower values in the exposure range based on extrapolated monitoring data and the higher values based on the highest Tier II modeled values for chlorpyrifos and Tier I modeled values for TCP. We believe actual exposures in vulnerable areas will be well below the high end of this range primarily because it is unlikely that chlorpyrifos usage in a watershed will be as pervasive as assumed in the modeling scenarios.

Maximum reported (and presumably actual peak) pesticide concentrations are typically less in reservoirs than in flowing water. However, peak multi-month or annual average concentrations are typically somewhat higher in reservoirs than in flowing water. Nevertheless, multi-month or annual mean concentrations in a reservoir should be less than the maximum reported concentrations in the flowing water feeding the reservoir. For this reason, we believe that high exposure levels for chlorpyrifos in reservoirs and lakes are more likely to be near 0.4 $\mu\text{g L}^{-1}$ (a high acute exposure level for streams) than the much higher modeled values. We have less confidence in saying this for TCP because of the total lack of monitoring data for TCP.

Part II: Termiticidal Uses

Ground-Water Sources

Results of ground-water monitoring studies confirm that contamination by chlorpyrifos is relatively rare and usually only occurs at levels in small fractions of a $\mu\text{g L}^{-1}$ from agricultural uses. However, the impacts from the use of chlorpyrifos to control termites can be much greater on a local scale.

Over 60 DowElanco 6(a) 2 submissions to the Agency from 1992 to 1995 indicate chlorpyrifos has been detected in drinking water wells, cisterns, or ponds in at least 12 states, including in Alabama, Illinois, Indiana, Maryland, New York, North Carolina, Ohio, South Carolina, Tennessee, and in several unidentified locations (Table 11). All of these incidents were shown to be associated with termiticide use in the area {97% within 100 feet of the wellhead, according to an investigation by the registrant: MRID 442350-01. Thomas, J.D. and D.M. Chambers. 1997. An analysis of factors involved in suspected well contaminations by chlorpyrifos-based termiticide emulsions (Dursban TC, Equity Termiticide)}. More recently (from December 1995 to April 1998), an additional 39 incidents have been reported. In fourteen of these incidents, wells were contaminated at levels of up to 458 $\mu\text{g L}^{-1}$. No information was given on the duration of contamination at these levels.

None of the modeling performed addresses impacts on drinking water that may arise from the termiticide use because there are no models available that can estimate concentrations in ground water that might arise from such use patterns. However, these uses pose particular risks for local contamination of ground water by chlorpyrifos parent. The data in Table 11 clearly demonstrate that concentrations of chlorpyrifos in ground water used for

drinking water can be more than 10,000 times higher than concentrations that result from other uses. Several factors are involved in this:

- (1.) The much greater persistence of chlorpyrifos in the concentrated applications used in termiticide treatments (refer to the earlier review of environmental fate for chlorpyrifos.)
- (2.) The concentrated applications used. For example, around the perimeter of a 80 x 20 foot building, the label allows for up to 13.2 pounds of chlorpyrifos active ingredient to be applied (Dursban TC Termiticide Concentrate, Label Code 113-58-004), with application of additional product along pipes outside the structure also permitted.
- (3.) The deep application of the product up to several feet below the ground surface.

We conclude that if chlorpyrifos is used for termite control within 100 feet of a drinking water well, then contamination at levels of up to about 2000 $\mu\text{g L}^{-1}$ is possible. Chronic exposure levels should be much lower, but residues can persist at detectable levels for at least 6 months (more data is needed to accurately estimate the potential for long-term exposure).

TABLE 11. Summary of private well contamination data associated with nearby termiticidal uses of chlorpyrifos (submitted to EPA per 6(a)2 reporting requirements).

Termiticide Use Well Data (chlorpyrifos was detected in all wells reported as being sampled)						
Data Source	Locations Sampled	# Wells	Detection limit, $\mu\text{g L}^{-1}$	Median detect, $\mu\text{g L}^{-1}$	Maximum detect, $\mu\text{g L}^{-1}$	Days to reach non-detectable levels
DowElanco (1992, MRID 430656 & various 6(a)2 submissions)	AL, IL, IN, KY, MD, MO, NC, NY, OH, SC, TN, VA	21	not given	81	916	7 to 160 for 12 wells
DowElanco (1993-4 6(a) data)	not given	9	not given	101	2090	17 for one well
DowElanco (1995 6(a) data)	not given	3	not given	66	76	not determined
DowElanco (1995 6(a) data)	AL, IA, KY	5?	not given	56	1634	19 to 188 for 3 wells
DowElanco summary report (1997, MRID 442350)	25 states, 84 wells with "detectable" (undefined) chlorpyrifos	213	not given	not given	not given	not given

Surface Water Sources

The EPA Water Incident Database has the following reports of chlorpyrifos in surface waters arising from termiticide uses:

TABLE 12. Summary of pond and stream contamination data associated with nearby termiticidal uses of chlorpyrifos (submitted to EPA per 6(a)2 reporting requirements).

Incident Code	State	Concentration, $\mu\text{g L}^{-1}$	Type of water
1002703001	OH	147	pond
1003505002	IN	35	pond
1002976001	AR	7090	lake
1002326001	IN	32.5	pond
1002713001	IN	214	pond
1002713001	TN	38	pond
1002995001	WV	41	stream
1003432002	GA	43	pond
1003432005	PA	64	creek
100359001	KY	37 to 40	pond
1006111	OH	1241	pond
1007150003	GA	>1270	pond
1007150005	IN	41	pond
1007150007	IN	79	pond
1007150008	VA	89	stream

No further details were provided on these detections so that it is impossible to analyze the significance of these reports in detail. Further investigation of the impacts of the termiticide use on water quality is needed to identify use scenarios that may pose an acute or chronic hazard to local drinking water quality.

Given the nature of termiticidal treatments (deep injection or placement in the soil), we would expect that direct runoff would be minimal. However, the NAWQA monitoring data now available do strongly imply that overall impacts of chlorpyrifos on surface waters from non-agricultural uses is at least as significant as from agricultural uses, with the % detections over $0.01 \mu\text{g L}^{-1}$, the 90th percentile values, and the 95th percentile values all higher in the streams draining primarily urban watersheds than in the streams draining primarily agricultural watersheds (Table 9).

For surface water, no separate exposure numbers have been calculated at this time for the termiticidal use since this is a highly localized use not as subject to runoff as other uses are and we do not have enough information to interpret the significance of the monitoring data in Table 12. The data do imply there may be a serious concern for local contamination at least of small bodies of water.